

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in Polymeric Compositions

5 We, CELANESE CORPORATION, of 525 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to improvements in polymeric compositions and, more particularly, compositions containing oxymethylene polymers.

15 Thermoplastic oxymethylene polymers of high molecular weight, above 20,000, are known which are of such high strength and thermal stability that they are valuable as materials for use in making shaped articles, for instance by extrusion or compression or injection moulding, especially where the articles must have higher mechanical strength and toughness and/or lower coefficient of friction than is possible when using the common fairly inexpensive thermoplastic materials. However, the surfaces of articles made from such polymers, while of a low coefficient of friction which is often desirable, cannot be provided with firmly adherent decorative coatings unless subjected to a pretreatment involving superficial etching and/or application to or formation on the surfaces of special sub-coats. Such operations add to the steps needed in making the shaped articles and hence to their cost and sometimes cause deterioration of physical properties of the polymer.

20 According to the present invention, an oxymethylene polymer of the kind referred to is blended with a minor proportion by weight

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of a polymer of an ethylenically unsaturated ester of a saturated carboxylic acid. It has surprisingly been found that the physical properties of the blend are not appreciably different from those of the oxymethylene polymer but that it is possible to make shaped articles from it to which decorative coatings adhere much more strongly than they do to articles made from the oxymethylene polymer alone.

The oxymethylene polymer may be a homopolymer, i.e. one in which the molecular chains consist solely of oxymethylene units, in which case it is preferred that the polymer should be one in which the terminal groups have been esterified or etherified, or a copolymer, i.e. one in which the molecular chains contain, besides oxymethylene groups, other groups dispersed along them derived from monomers such, for instance, as lactones, carbonates, cyclic anhydrides, glycidyl ethers, alkylene oxides, aldehydes higher than formaldehyde and ethylenically unsaturated compounds, e.g. vinyl ethers, styrene, vinyl acetate, vinyl methyl ketone or acrolein. As is known, the introduction into the molecular chains of a small proportion, e.g. up to 20 mole per cent, of groups having adjacent carbon atoms forming links in the chains endows the polymer with increased thermal stability without detracting from its value as a thermoplastic moulding material. Copolymers of 80 to 99 mole per cent of trioxane and 1 to 20 mole per cent of monomers providing oxymethylene groups, e.g. ethylene oxide or dioxolane, are particularly satisfactory for use according to the invention. The polymers may be derived from more than two monomers, for instance very useful terpolymers are those obtainable by copolymerising trioxane, 1 to 20 mole per cent of a monomer providing oxy-

ethylene groups and 0.01 to 7 mole per cent of a monomer providing cross-links between different molecular chains, for instance compounds having at least two epoxy rings, at least two dioxacyclo rings or at least one epoxy ring and at least one dicyclo ring, and compounds having at least two oxa groups such as dialdehydes and diketones, e.g. butadiene dioxide, resorcinol diglycidyl ether, butane diol diglycidyl ether, ethylene glycol diglycidyl ether, butane diol diglycidyl ether, ethylene glycol diglycidyl ether, vinyl cyclohexane diepoxide or pentaerythritol diformal.

The polymeric ester blended with the oxymethylene polymer may be derived from an alkenyl alkanoate having, for instance, up to about 12 carbon atoms, and is preferably derived from an ester of an alkanol having up to 6 carbon atoms. Polymers of vinyl acetate, allyl acetate and the corresponding propionates and butyrates are examples of suitable esters. Copolymers comprising units derived from a mixture of the foregoing monomers may be used as may polymers derived from mixtures thereof comprising also a minor proportion of one or more other vinyl or vinylidene monomers, for instance vinyl halides, e.g. vinyl chloride, aryl alkenes, e.g. styrene or alpha-methyl styrene, esters of unsaturated carboxylic acids, e.g. dibutyl fumarate, dibutyl maleate, methyl crotonate, ethyl acrylate, methyl methacrylate or t-butyl acrylate, vinyl esters of aromatic carboxylic acids, e.g. vinyl benzoate, unsaturated ethers, e.g. n-butyl vinyl ether or phenyl vinyl ether, alkenyl carboxylic acid nitriles, e.g. acrylonitrile or methacrylonitrile, alkenyl carboxylic acid amides, e.g. acrylamide or methacrylamide, vinyl substituted hetero - N - cyclics, e.g. N - vinyl - 2 - pyrrolidone or vinyl pyridines, or olefines, e.g. ethylene, propylene, isobutylene, 1 - butene, 3 - methyl - 1 - butene or 4 - methyl - 1 - pentene. Generally, however, the polyvinyl alkanoates contain at least 50 mole per cent, and preferably at least 75 mole per cent, of units derived from the alkenyl alkanoates having up to about 18 carbon atoms.

While the blend proportions may, in general, vary from approximately 1 to 25 weight per cent of the polymeric ester, certain proportions are preferred in specific embodiments, e.g. the 5 to 10% level appears to provide optimum mechanical properties. Homogeneity of all melts was excellent and complete clarity was apparent at levels as high as 20 weight per cent. Compression moulded samples exhibited excellent adhesion to coatings over the entire range, even at the lower levels, e.g. 1 to 5 weight per cent, without any treatment after moulding. Injection moulded samples prepared at conventional mould temperatures for oxymethylene polymers, e.g. 90 to 95°C., required baking, e.g. at 120°C.

for half an hour, to develop optimum adherence. Surprisingly, however, samples containing 10% or more of the polymeric ester met all adherence tests without any treatment after moulding when injection mould temperatures were raised to higher levels, e.g. 120°C. In fact, the improvement was obtained with samples containing 10 to 15% polymeric ester at higher mould temperatures, although material temperatures were somewhat decreased.

Infra red examination by attenuated total reflection at the surface of 60 mil slabs injection moulded at conventional oxymethylene polymer mould temperatures shows less than one-half as much as the polymeric ester than at a surface exposed by shaving off a 10 mil layer. This effect is believed to be due to preferential surface solidification of the oxymethylene polymer at the relatively cold walls of the mould, due to the great difference between the melting points of the oxymethylene polymer (e.g. 162°C. for a commercial copolymer sample) and the second order glass transition temperature of the polymeric ester (e.g. 30°C. for polyvinyl acetate). Apparently higher mould temperatures overcome the effect of the preferential precipitation and provide the requisite blend composition for satisfactory adherence of coatings. In fact, control of mould temperatures would appear to permit the regulation of the proportion of polymeric ester at the surface and hence of the degree of adherence. Thus, portions of moulded articles, e.g. bearings, bolts or screws, requiring the full strength and surface characteristics, e.g. lubricity, of the oxymethylene polymer, could be provided by bringing the polymeric ester to the surface of only those areas where an adherent decorative coating is required by using a mould temperature over those areas high enough to produce the desired effect, e.g. 110° to 130°C.

A baking step after moulding improves the adhesion of subsequently applied coatings and according to a further aspect of the invention a moulded article comprising the blend of the oxymethylene polymer and, preferably, from 5 to 10 weight per cent of the polymeric ester, is subjected to temperatures of 115° to 160°C for periods of at least 10 up to about 45 minutes.

Variation in the molecular weight of the polymeric ester does not appear to affect the result achieved to any great extent, but intermediate molecular weight polymeric esters appear to result in better mechanical properties and accordingly are preferred. More specifically, while polymeric esters having molecular weights represented by viscosities of 1.0 to 25.0 cps (measured in a solution of 86.1 grams of polymer in sufficient benzene to make 1 litre) may be employed, those exhibiting viscosities in the range of 10 to 20 cps are preferred. Molecular weights are approxi-

mately 1000 times the viscosity values in cps measured in solutions of the concentration indicated. A particularly preferred species is a vinyl acetate homopolymer containing no more than 2.0% hydroxyl and having a molecular weight of approximately 20,000.

The compositions may be prepared by conventional blending methods, e.g. co-solution and co-precipitation, dry-blending of the powdered ingredients or co-extrusion, but melt-blending, wherein at least one component is maintained in fluid state, is preferred for ease of operation and homogeneity of product. Thus, the blending is preferably carried out at a temperature above the melting point of at least one of the blend components, generally between about 100°C. and 220°C. and preferably between about 150°C. and 200°C., and vigorously mixing and shearing for a period between 1 and 20 minutes until substantial homogeneity has been achieved. If desired, a blend can be made containing a higher proportion of one ingredient than is desired in the final product and more of the other ingredient added later. Usually, a high shear mixing device, such as a 'Brabender Plastograph' or 'Banbury' mixer, is employed. The blending may, however, also be carried out in a roll mill apparatus having oppositely rotating hollow cylindrical rolls of, for example, 12 inches diameter, driven at a speed in the range of 20 to 40 revolutions per minute, and steam heated to a temperature in the range of 165°C. to about 195°C.; the cylindrical rolls have a variable clearance ranging down to a few thousandths of an inch, this clearance being varied during the course of the milling. A typical run involves charging the blend components to the rolls with a load time of 3 to 5 minutes and rolling for 4 to 5 minutes to produce a melt. The blend, which adheres to the rolls, is kneaded with reduced clearance between the rolls for a period of approximately 5 minutes and then cut and cooled.

It is to be understood that conventional additives, including stabilisers, lubricants, fillers such as glass powder or chopped strand, finely divided copper, titanium dioxide and dyes may be incorporated into the blend. Such additive usually include stabilisers for the oxymethylene polymer, for instance an amidine compound, e.g. melamine or cyanoguanidine, together with a phenolic anti-oxidant, preferably an alkylene bisphenol, e.g. 2,2'-methylene bis(6 - t - butyl - 4 - methyl phenol).

Moulded articles of the blend compositions may be made by any conventional methods, including compression moulding, injection moulding, vacuum forming, impact forming and blow moulding. These articles may be decorated with, for instance, paints, varnishes or metallic coatings, and may serve as bases for laminates with organic film-forming polymeric substances. Adherence is also important

in applications where no decoration as such is applied but where labels are to be affixed or other materials fixedly attached to the surface as by gluing, and these applications are also envisaged. Representative coatings include nitrocellulose formulations, automobile paints, e.g. acrylic base lacquers or thermosets, alkyl-melamines, organic resins such as the vinylidene chloride interpolymers with, for instance, acrylonitrile, acrylic esters, e.g. methyl acrylate, itaconic acid, crotonic acid or maleic acid, phenolics such as t-butylated phenol-formaldehyde, epoxy resins, e.g. of bisphenol A and epichlorhydrin, polyurethanes, e.g. of toluene di-isocyanate and ethylene glycol adipate, polyesters, e.g. polyethylene terephthalate, polyvinyls (such as ethylene/vinyl acetate copolymers, and metallic coatings such as may be deposited from for instance, copper or chromium plating formulations.

Laminates with any otherwise suitable organic resin may be readily prepared, including multi-ply structures with more than one type of resin layer other than the blend of this invention. Representative of such organic resins are cellulose acetate, cellulose propionate, cellulose acetate butyrate and cellulose propionate butyrate, the polyesters such as polyethylene terephthalate, the polyvinylidene chlorides and the polyolefines, e.g. polypropylene.

The standard tests of adhesion employed for the purposes of this specification and claims are elsewhere briefly described as the 'Scotch' Tape test and the scratch test. Scotch Tape is a Registered Trade Mark. The 'Scotch' Tape test is carried out by removing surface grease from an injection moulded 60 mil slab or a compression moulded disc with a carbon tetrachloride rinse, wiping and drying, applying the desired coating in a thin uniform coat, drying, e.g. in air overnight, scribing the dried coated surface with a razor blade in a pattern of 1/16 inch squares over an area about 3/4 to 1 inch square, applying an adhesive tape such as 'Scotch' brand tape to the scribed surface and then quickly removing the tape in one motion. If any of the coating in the cross-hatch pattern is removed with the tape the sample is considered to have failed the test.

The scratch test is carried out by attempting to scratch with removal of the coating the dried coated surface by applying the edge of a rounded circular metallic object, e.g. a coin, to the surface with moderate pressure.

In the following Examples, which illustrate the invention, all melt index values were taken in accordance with ASTM D-1238-57T, under Condition E (designated "1x") or Condition F (designated "10x"). Thermal decomposition rate constants (K_D) were measured on 5 gm. samples of the oxymethylene polymers used which all contained 0.5% 2,2'-

methylen bis(4 - methyl - 6 - tertiary butyl phenol), and 0.1% cyanoguanidine as stabilisers. The samples, in the form of 1/8 inch pellets, were placed in a circulating air oven maintained at 230°C., re-weighing after a 45 minute test period, and expressing the loss in weight as an average rate in units of weight per cent per minute.

EXAMPLE 1

A homogeneous blend of 85 parts of an oxymethylene polymer containing about 2.0% of oxyethylene units and having a melt index (1x) of 9.0 decigrams per minute and 15 parts of a vinyl acetate polymer (1.7% hydroxyl; inherent viscosity in benzene of 1.2) was prepared by mixing the components in a 'Plastograph' at 190°C. for 10 minutes.

A film was prepared from the clear blend melt and no gels or other inhomogeneities were evident in the film. The film was painted with a commercial acrylic base automobile paint and dried overnight. Adhesion of the paint was tested by creasing the films through 180° when very little paint break was apparent.

A portion of the blend was compression moulded into a 2 inch disc at 190°C., and painted. The disc was dried overnight, scribed with a razor blade into 1/16 inch squares and the 'Scotch' Tape test applied. Paint adhesion was excellent, evidenced by the complete absence of paint removal as the tape was pulled off the disc.

In contrast with the results obtained in the above Example, a film prepared from the same oxymethylene polymer alone, when creased, showed a complete loss of paint at the crease while a compression moulded disc

made from the oxymethylene polymer alone lost a substantial part of paint under the 'Scotch' Tape test, both film and disc being painted in the same way as those made from the blend.

EXAMPLE 2

Blends of an oxymethylene copolymer containing approximately 2% of oxyethylene units and a polyvinyl acetate ('AYAT' manufactured by Union Carbide) containing 1.0, 3.5, 5.0 and 10.0 weight per cent, respectively, of polyvinyl acetate were prepared by melt mixing in a 'Banbury' mixer at 160°C. for 6 minutes. All samples exhibited thermal decomposition rate constants of less than 0.015 weight per cent per minute. Compression moulded specimens (2x1/8 inch discs) were prepared, in a press with provision for air cooling moulds at 190°C. and 240°C. Injection moulding was carried out in a Moslo 1 ounce injection machine at 238°C. material temperature, 93°C. mould temperature and a pressure of 25,000 pounds per square inch with a 60 second cycle. The compression moulded samples in each instance and without further treatment passed the 'Scotch' Tape test when spray painted with an acrylic base automobile paint. The injection moulded samples similarly passed the test when heat treated at temperatures ranging from 120°C. for the 5 and 10% samples to 155°C. for the 1 and 3.5% samples. Physical properties of the injection moulded samples were excellent, typical figures for the 1 and 10% specimens being given below together with the figures for a control sample made from the oxymethylene polymer alone.

	Control 100% Copolymer	1.0% PVAc	10.0% PVAc
Izod Impact (Notched) foot pounds per inch	1.17	1.35	7.19
Tensile Strength psi	8,760	8,440	7,450
Tensile Modulus psi x 10 ⁴	0.394	0.430	0.405
Tensile Impact foot pounds/inch	76.4	100.2	91.2
Elongation %	38.8	34.0	42.3
Vicat softening Temperature °C.	161	160.2	160
PVAc=polyvinyl acetate			

Similar results were obtained with 5, 10 and 15 per cent samples employing a polyvinyl acetate having an inherent viscosity (ASTMD-1243-58T, Procedure A) of 0.12 and a softening point of 32°C.

The samples also passed the scratch test after heat treatment.

EXAMPLE 3

15 and 25% blends of polyvinyl acetate (having an inherent viscosity according to Procedure A of ASTMD-1243-58T of 0.69, a softening point of approximately 86°C. and a

tensile strength of 4200 psi) with an oxymethylene copolymer containing 2.0% of oxyethylene units and having a melt index (1x) of 2.5 decigrams per minute were prepared in a 'Banbury' mixer at 160°C by mixing for 6 minutes. 10x/1x melt index ratios were 28.6 and 37.8, for 1x values of 3.56 and 4.77, respectively. A 3x3x50 mil injection moulded slab (238°C. material temperature, 98°C. mould temperature, 25,000 psi 60 second cycle) prepared from the 25% blend passed the 'Scotch' Tape test without further treatment. The 15% composition required

heat treatment. A similar run employing a high I.V. (1.13) polyvinyl acetate at 10 and 25% concentrations gave the same results.

EXAMPLE 4

- 5 A series of blends of polyvinyl acetate (inherent viscosity 0.69) and an oxymethylene-oxethylene copolymer (melt index (1x) of 9.0 decigrams per minute) ranging in composition from 8 to 15 weight per cent of the polyvinyl acetate were prepared, and injection
10 moulded at a material temperature of 227°C., a mould temperature of 120 to 125°C. and a pressure of 25,000 psi with a 60 second cycle. The 10, 11, 12, 13, 14 and 15%
15 samples all passed the 'Scotch' Tape adhesion test without further treatment. The 8% sample required a heat treatment (120°C. for $\frac{1}{2}$ hour) to pass the test. All samples passed the scratch test after heat treatment at 120°C.
20 for $\frac{1}{2}$ hour.

WHAT WE CLAIM IS:—

1. A thermoplastic composition comprising an oxymethylene polymer of molecular weight above 20,000 and which can be formed
25 into shaped articles to which coatings adhere more strongly than to articles made from the polymer alone, said composition comprising the polymer blended with a minor proportion by weight of a polymer of an ethylenically
30 unsaturated ester of a saturated carboxylic acid.

2. A thermoplastic composition according to Claim 1, wherein the polymeric ester is polyvinyl acetate.

3. A thermoplastic composition according to Claim 1 or 2, wherein the composition contains from 1 to 25% by weight of the polymeric ester. 35

4. A thermoplastic composition according to Claim 1, 2 or 3, wherein the oxymethylene polymer contains 1 to 20 mole per cent of oxymethylene groups. 40

5. A thermoplastic composition comprising an oxymethylene polymer containing 1 to 20 mole per cent of oxymethylene groups and polyvinyl acetate, substantially as described in any of the Examples. 45

6. A thermoplastic composition, substantially as hereinbefore described and shaped articles made therefrom. 50

7. Method of rendering articles made from compositions as claimed in any of the preceding claims more strongly adhesive to coatings comprising heating the articles to a temperature of 115° to 160°C which is below the softening point of the composition for a period of from 10 to 45 minutes. 55

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